Update on the Fast GC/Luminol System for NO_2 and PAN Measurements

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Abstract

The fast GC/Luminol instrument for the rapid simultaneous detection of NO_2 and PAN has been redesigned to be small and lightweight. It is contained in a standard 19 inch rack mountable case with a total weight of 35.5 pounds (not including laptop and carrier gas bottle). It is run from a laptop computer under a Labview environment. The software synchronizes injection and data collection, eliminating the need for hardware to actuate the injection valve. Both raw and integrated Data is stored automatically in spreadsheet format. The instrument can make use of Matheson Minimat gas cylinders (12in. X 2 in; 4 lbs) for both carrier and standard to minimize size and weight.

The reaction cell has been redesigned to minimize dead volume and the interface between the cell and PMT is constructed to minimize stray light. All DC power is supplied by one internal power supply.

The new design was field tested on the NOAA Twin Otter during the BRACE campaign (May, 2002) and operated unattended through most of the study. These results are compared to those obtained in central California during the CCOS field campaign (July, 2000) with the previous instrument design.

This new design allows for detection limits of 10 ppt for PAN with a PAN/NO2 sensitivity Ratio of 1.4 depending on the Luminol conditions.

Analytical Determination of Reactive Nitrogen Species:

Chemiluminescent Reaction with Ozone:

$O_3 + NO \rightarrow NO_2^* + O_2$ (590 – 3000 nm; λ_{max} = 1270nm)

If O_3>>NO = NO detection

If $NO_2 \xrightarrow{\Delta} NO$ = NO_2 detection (also PANs, RNO_3, NH_3, HNO_3, N_2O_5, $ClNO_x$, HONO)

If $NO_2 \xrightarrow{h\nu} NO$ = NO_2 detection (also HONO, NO_3, HO_2NO_2)

PEROXYACYL NITRATES

- Organic oxidants having the general chemical structure RC=OO-O-NO_2

- Most common PANs are peroxyacetyl nitrate (PAN; R=CH_3-), peroxypropionyl nitrate (PPN; R=CH_3CH_2-), and peroxybutyryl nitrate (PBN; R=$CH_3CH_2CH_2$-).

- PANs are in thermal equilibrium with the peroxyacetyl radical (RC=O-OO.) and NO_2 $\Rightarrow$ trapped peroxy radicals.

  $\Rightarrow$ indicator species of the photochemical age of an air parcel.

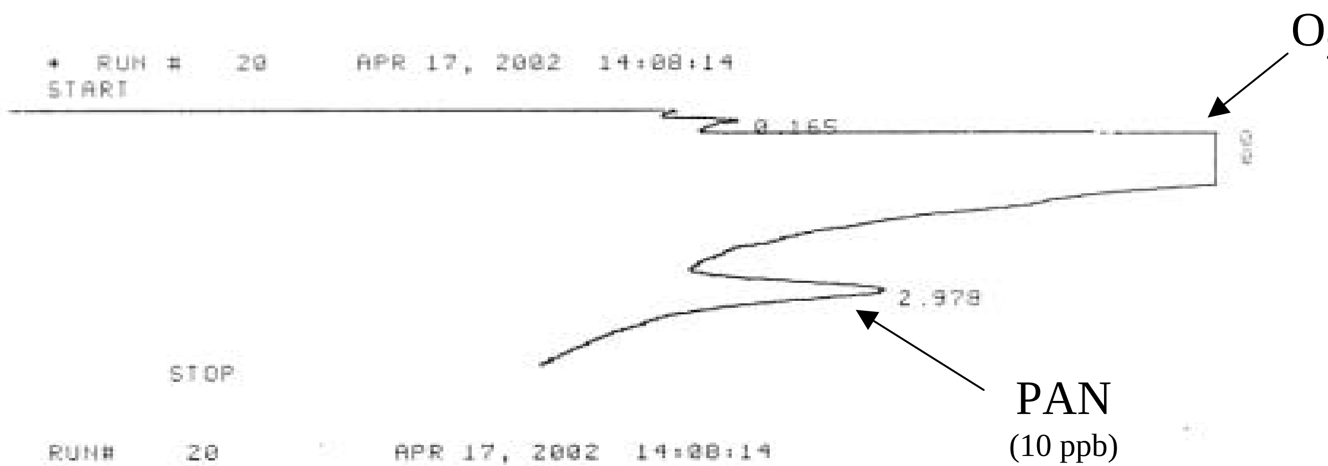
  $\Rightarrow$ important as a vehicle for long-range transport of NO_2.

  $\Rightarrow$ leading to the formation of regional ozone and other oxidants.

Analytical Determination of Peroxyacyl Nitrates (PANs):

$R{=}OO\text{-}O\text{-}NO_2 \rightarrow RC{=}O\text{-}OO\bullet + NO_2$

<u>Gas Chromatography with Electron Capture Detection:</u>



RUN# 20 APR 17, 2002 14:08:14

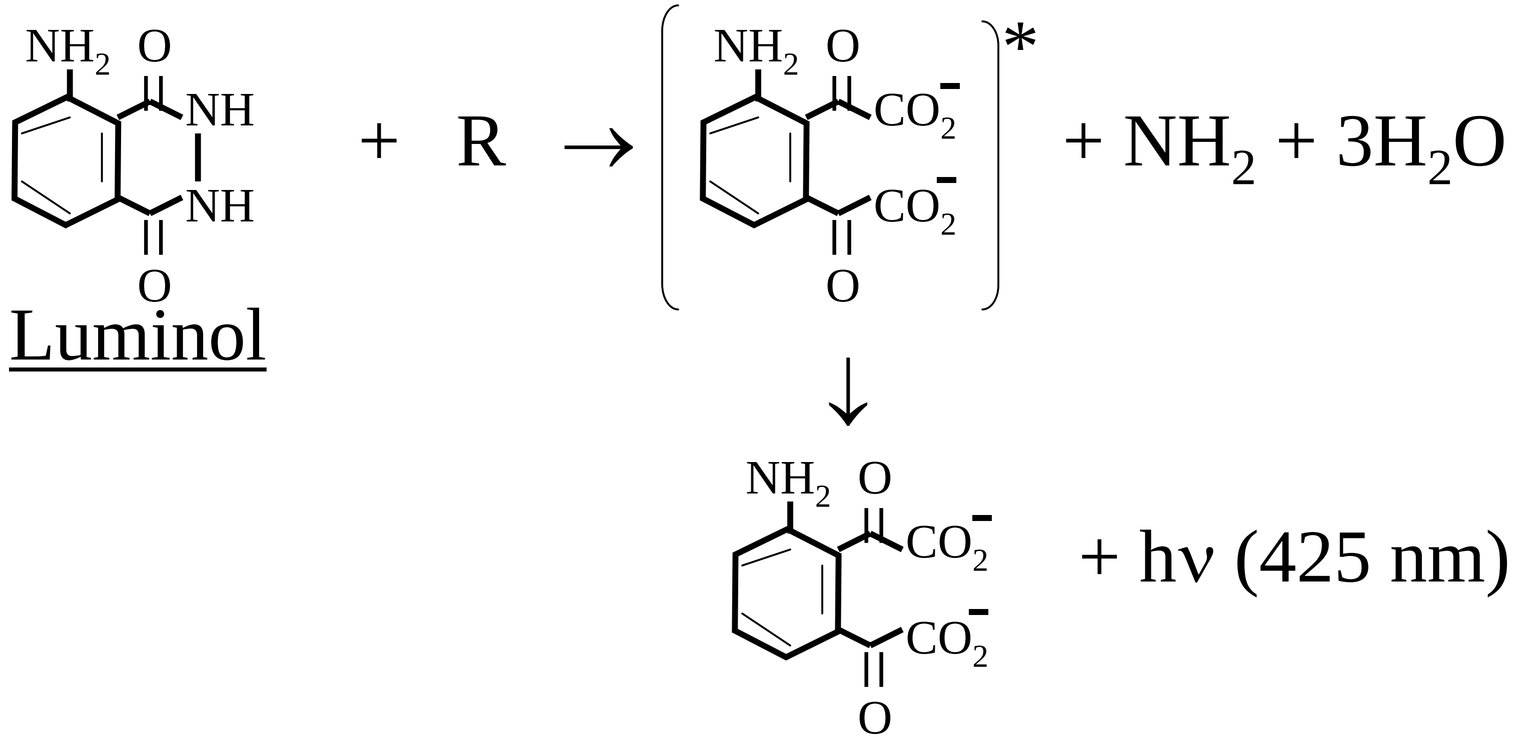
AREA%

RT	AREA	TYPE	WIDTH	AREA%
.165	3073	PP	.107	5.64610
.390	4673	PB	.003	8.58581
2.978	46681	I BP	.467	85.76810

TOTAL AREA= 54427
MUL FACTOR=1.0000E+00

Also O_2, CFC's, H_2O have strong signals. – background limits analysis speed (typically 15 - 30 min.) before signal returns to baseline values.

Chemiluminescent Reaction with Luminol:

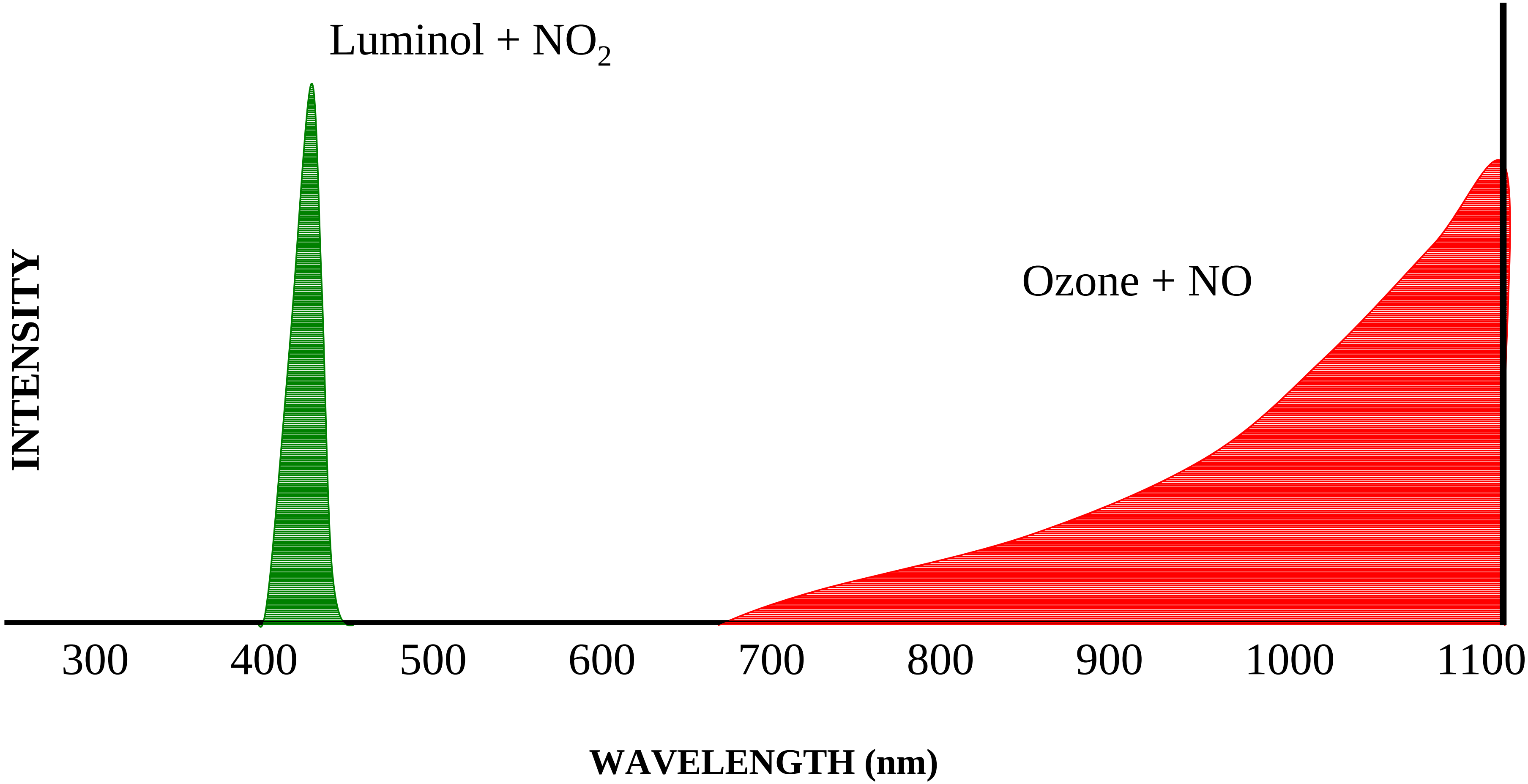


R = NO_2, PANs, H_2O_2, amino PAHs, metal ions, enzymes, carbohydrates

R can be selected by changing the pH, ionic strength or including a catalyst in the luminol solution.

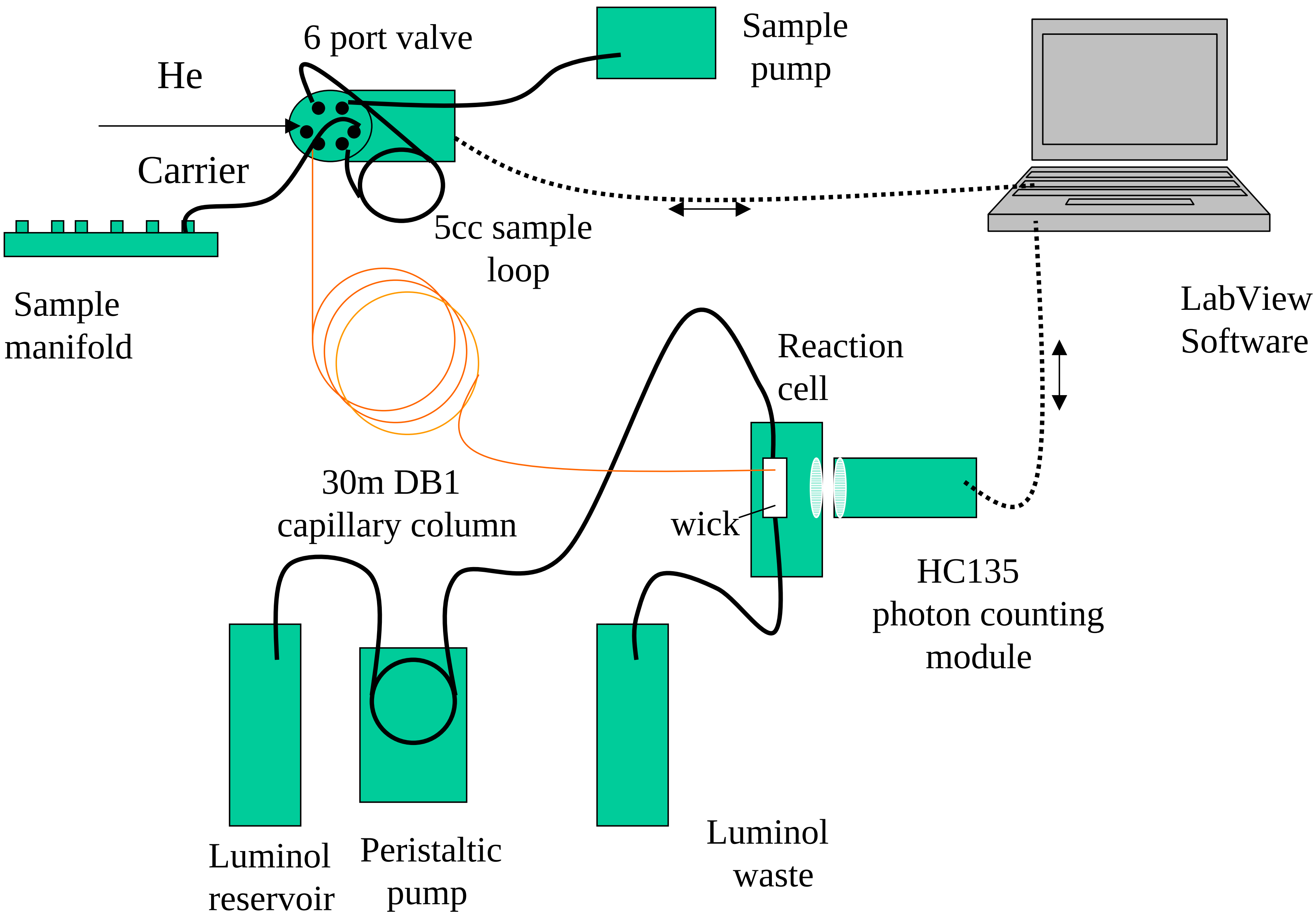
Light intensity $\propto$ R concentration

Chemiluminescent Emission Regions



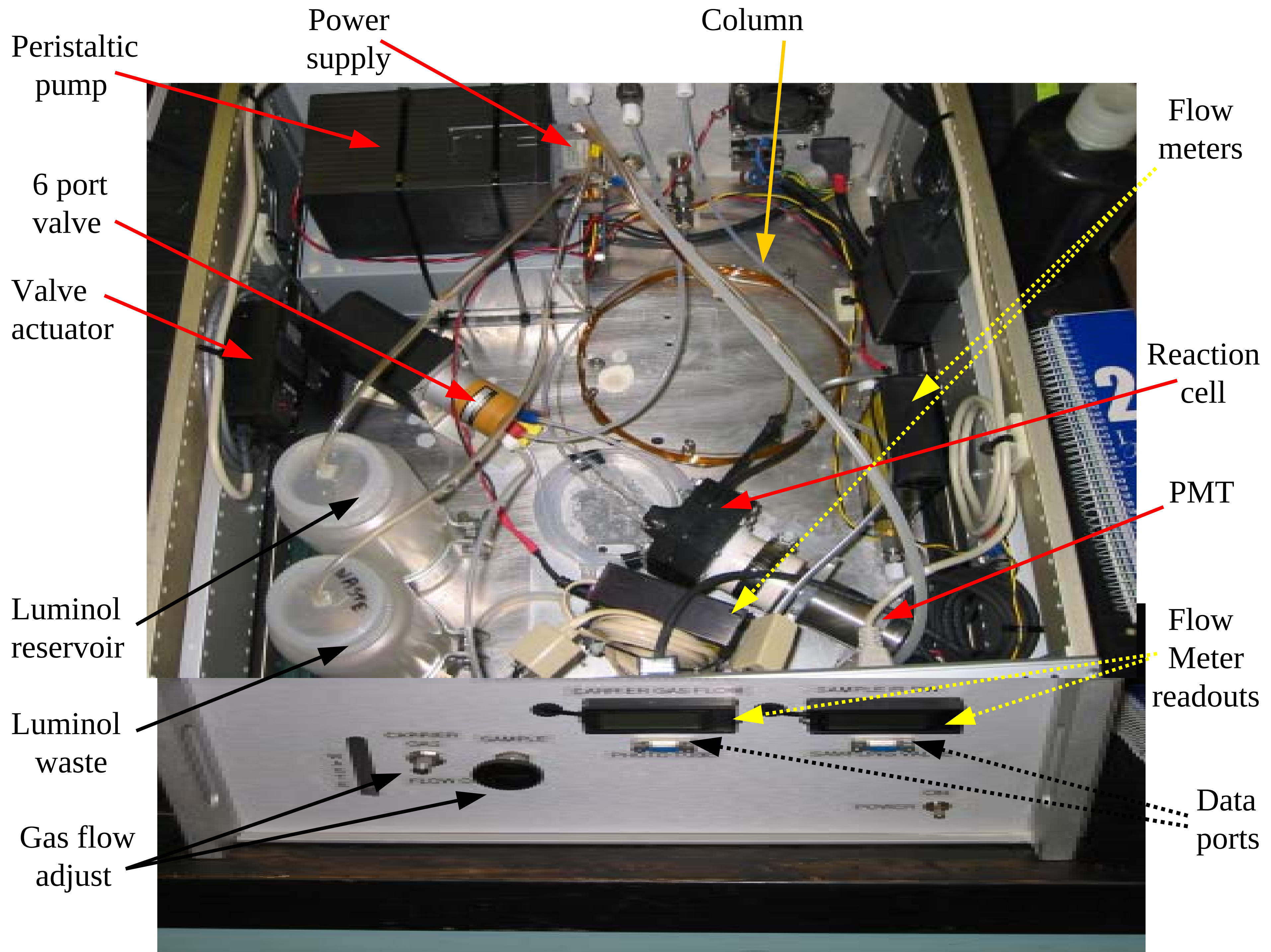
Luminol Chemiluminescence is more sensitive than ozone chemiluminescence for reactive nitrogen species because the available photo multiplier detectors are more sensitive in the region of emission.

Fast GC with Luminol Detection

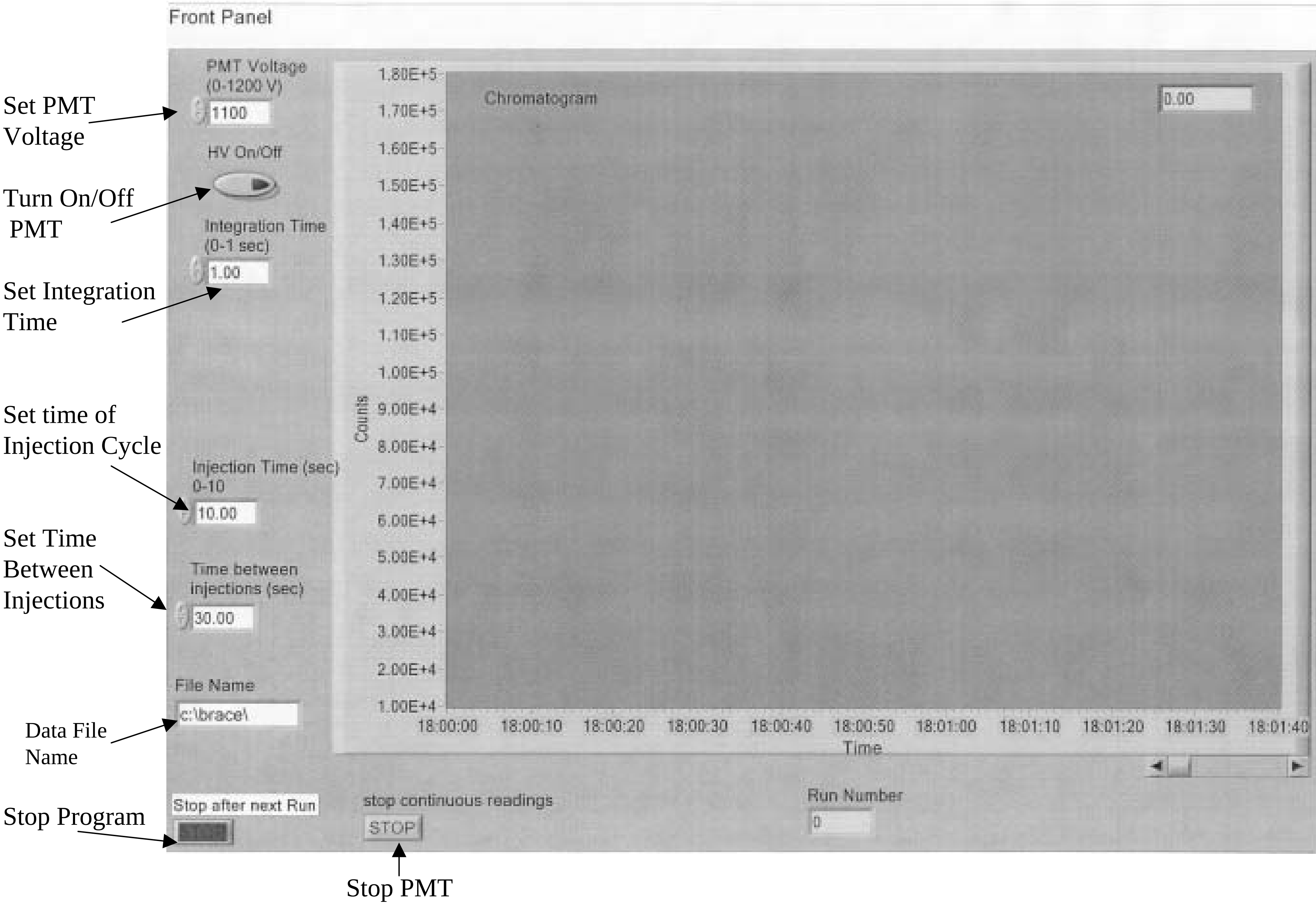


Hamamatsu HC135-1 Photon Counting Module

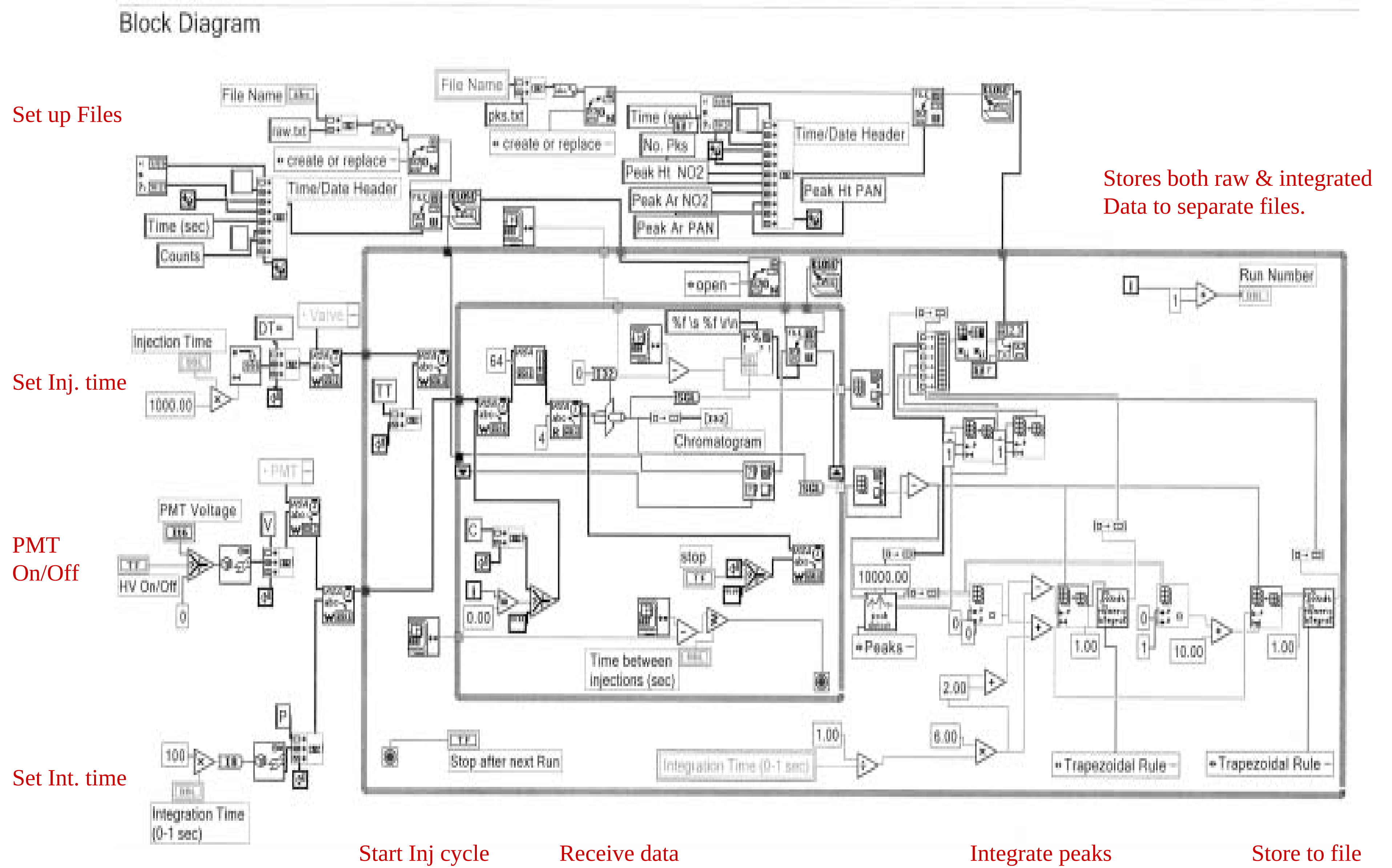
	Specifications	Luminol Chemiluminescence
Spectral Range =	300-650 nm	375-550 nm
Peak Wavelength =	400 nm	425 nm
Counting Efficiency =	22 %	
Dynamic Range =	2×10^6	
Linearity =	$0 \rightarrow 2 \times 10^6$	Range = DL $\rightarrow$ 160 ppb
Spectral Sensitivity =	4.3×10^5 cps/pW	
Maximum Light Input =	70 pW	$\cong$ 30 Mcps
Dark Count =	100 s^{-1}	$\cong$ 8 ppt
Baseline Stability =	11 %/^{o}C	$\Rightarrow$ 5oC = 55 cps drift
Response =	0.1 %/^{o}C	
Optimum Integration Time =	1 s	
Smallest Interval =	10 ms	
Dimensions =	1¼ X 4¾ in	
Window Size =	1 in	


Peristaltic pump
Power supply
Column
Flow meters
6 port valve
Valve actuator
Reaction cell
PMT
Luminol reservoir
Luminol waste
Gas flow adjust
Flow Meter readouts
Data ports

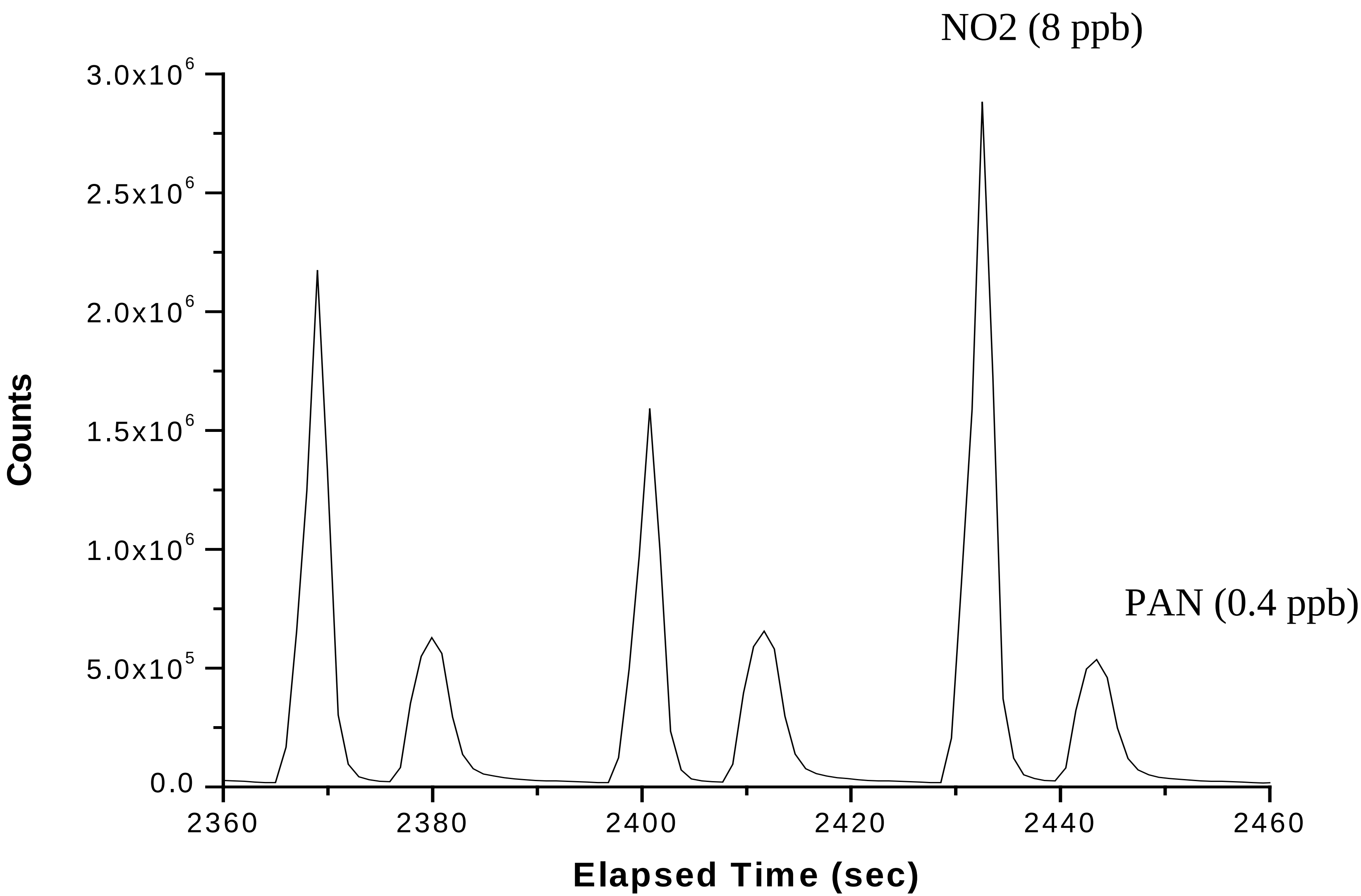
Labview Virtual Instrument Front Panel



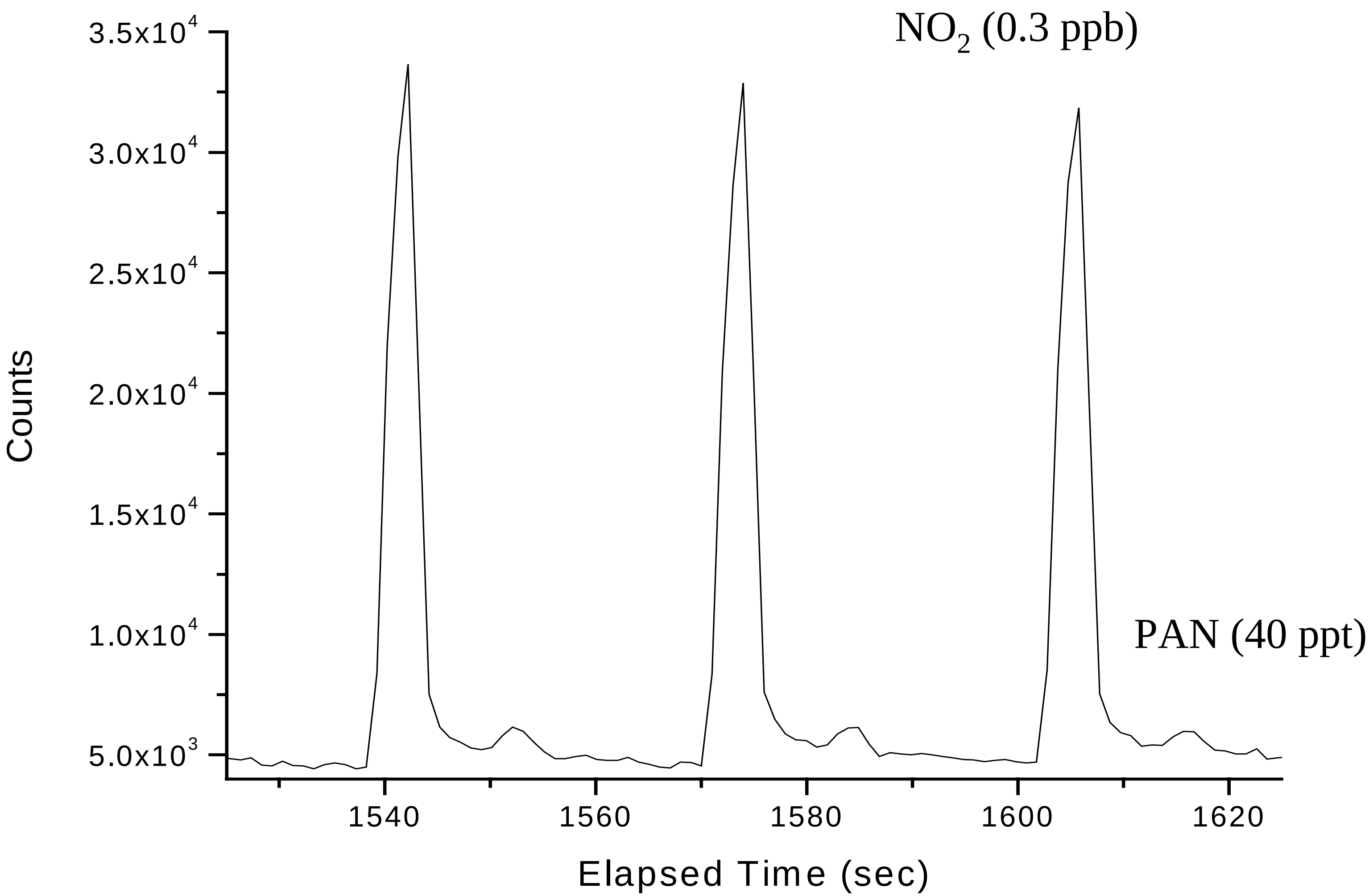
Labview Virtual Instrument Block Diagram



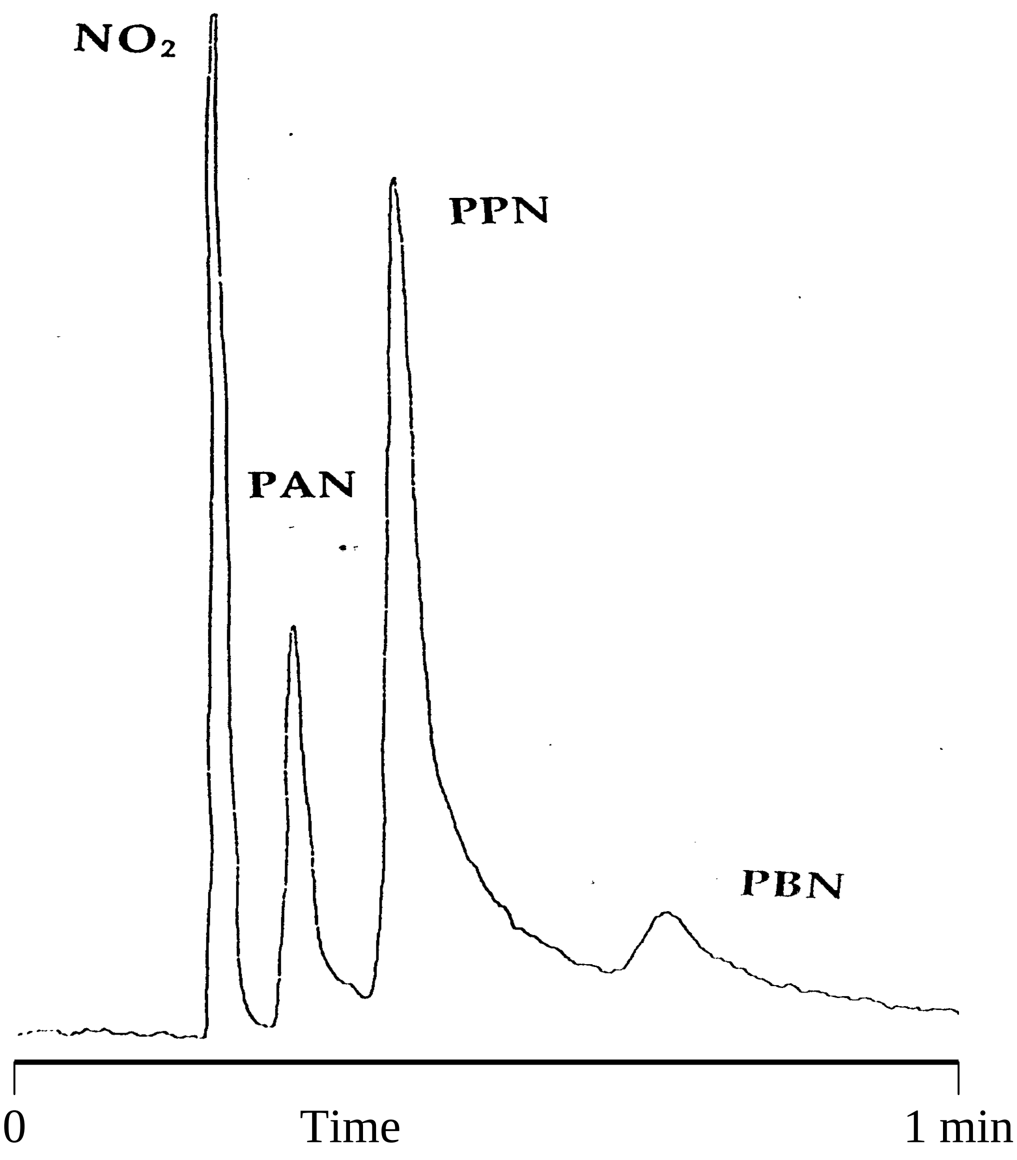
PAN & NO_2 Standards



NO_2 & PAN in Room Air



NO$_2$, PAN, PPN, PBN Standard Separation
Luminol Chemiluminescence Detection

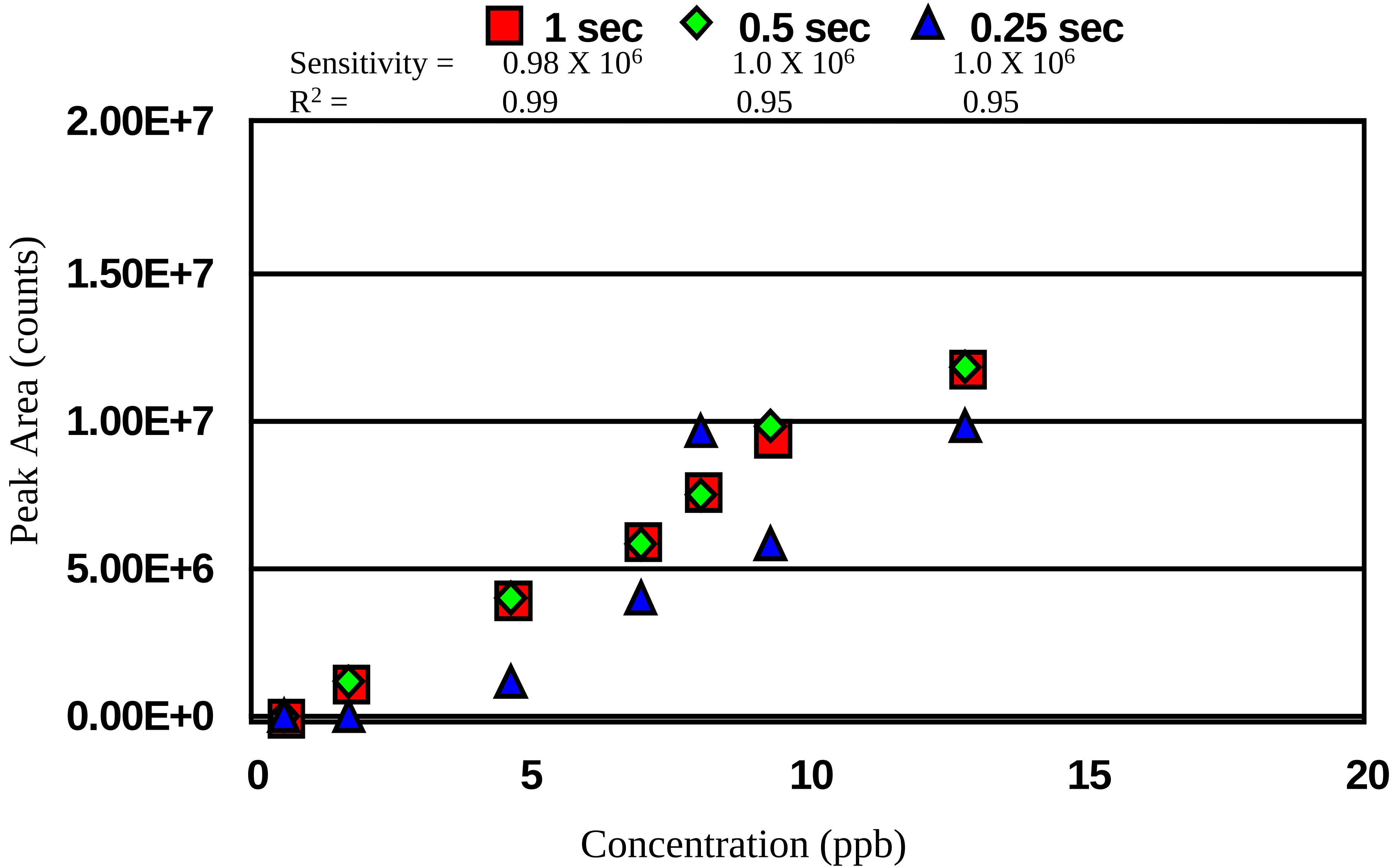


NOAA Twin Otter Inside Cabin

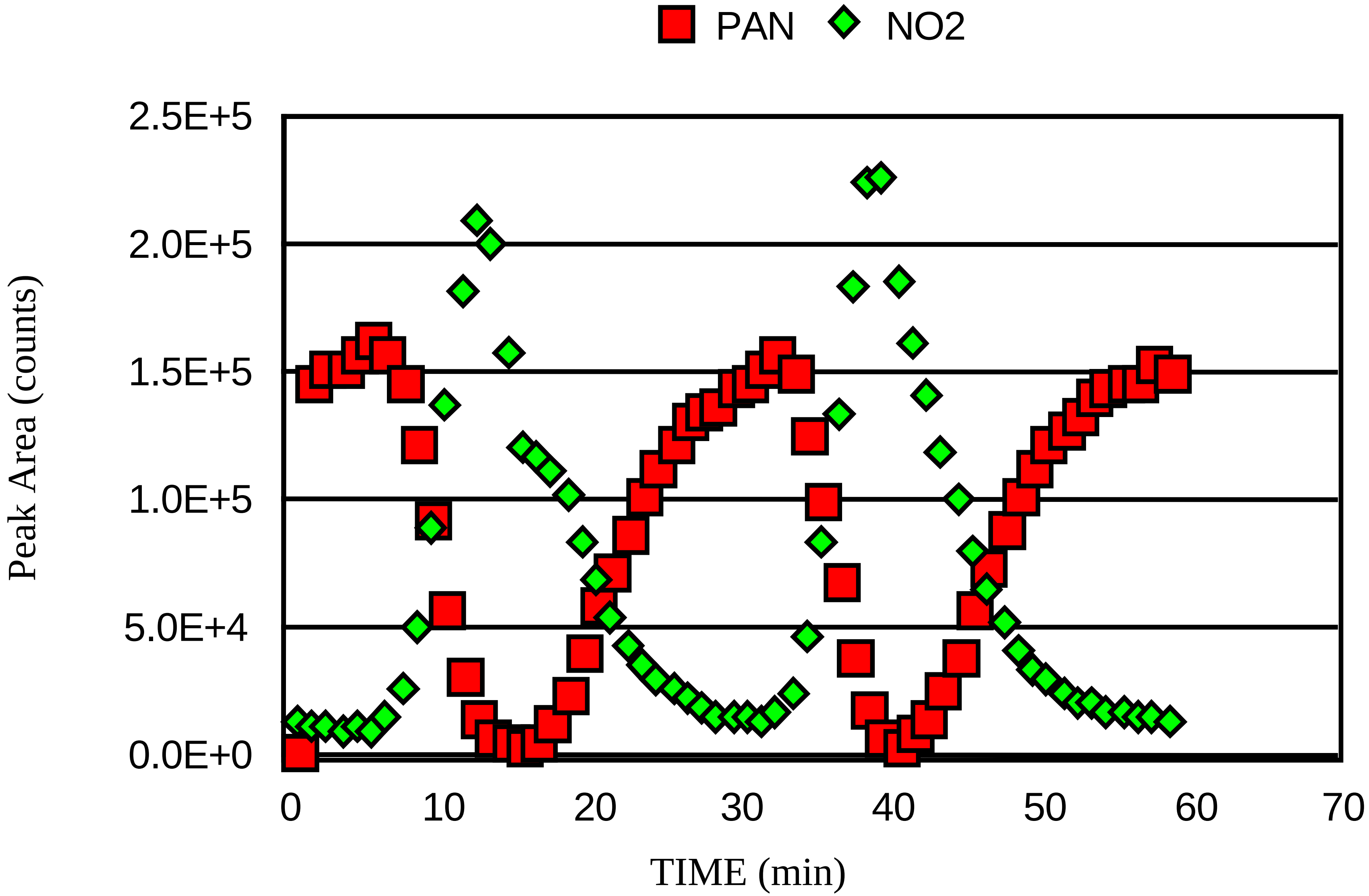
Laptop with Labview Software

PAN/NO2 Instrument
Luminol Chemiluminescence

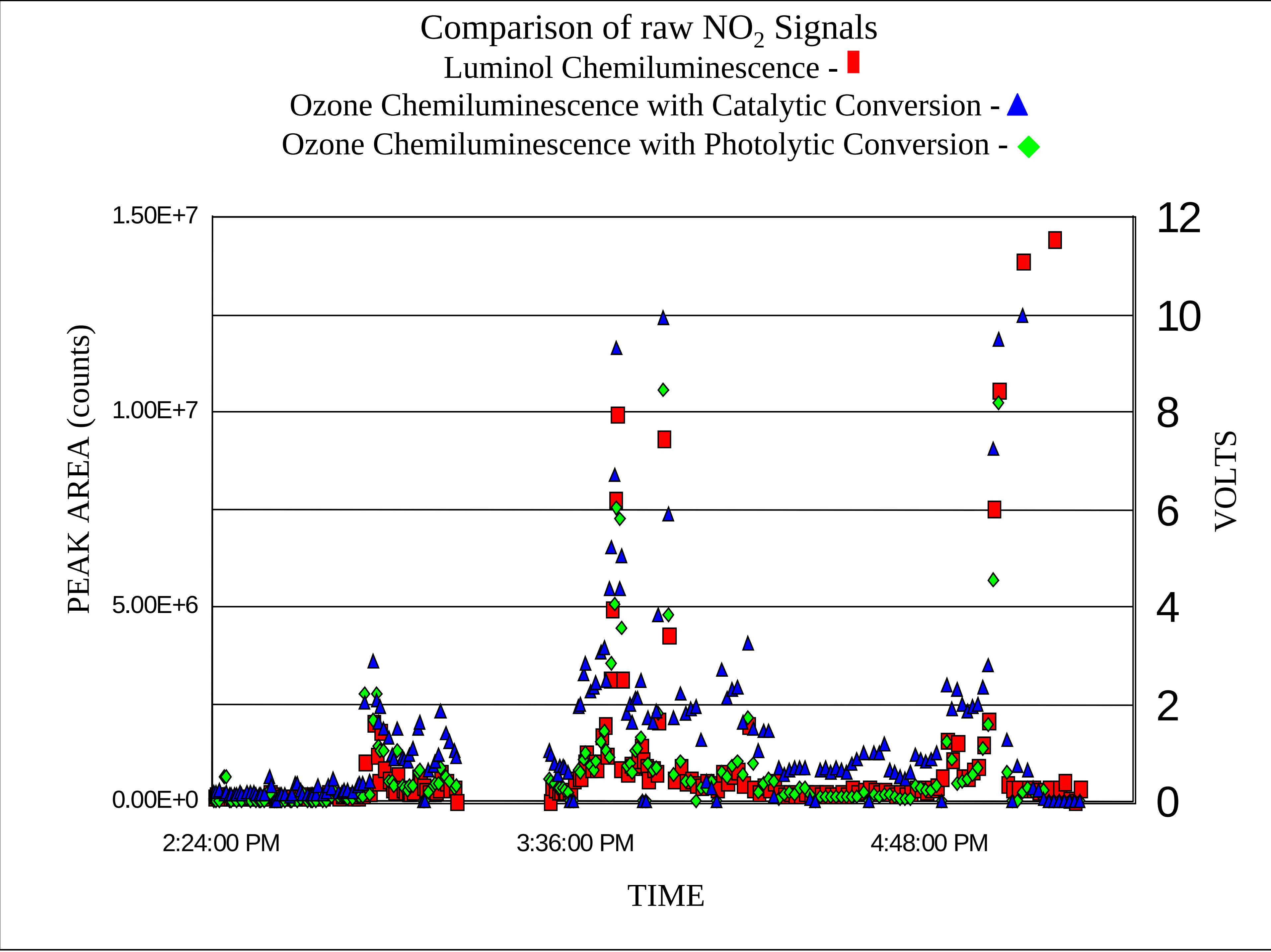
Calibration of the fast GC-luminol instrument for NO_2 at 1-sec, 0.5-sec, and 0.25-sec integration times.



Thermal decomposition of PAN samples to NO_2, followed by reformation of PAN, as measured by the fast GC-luminol instrument.

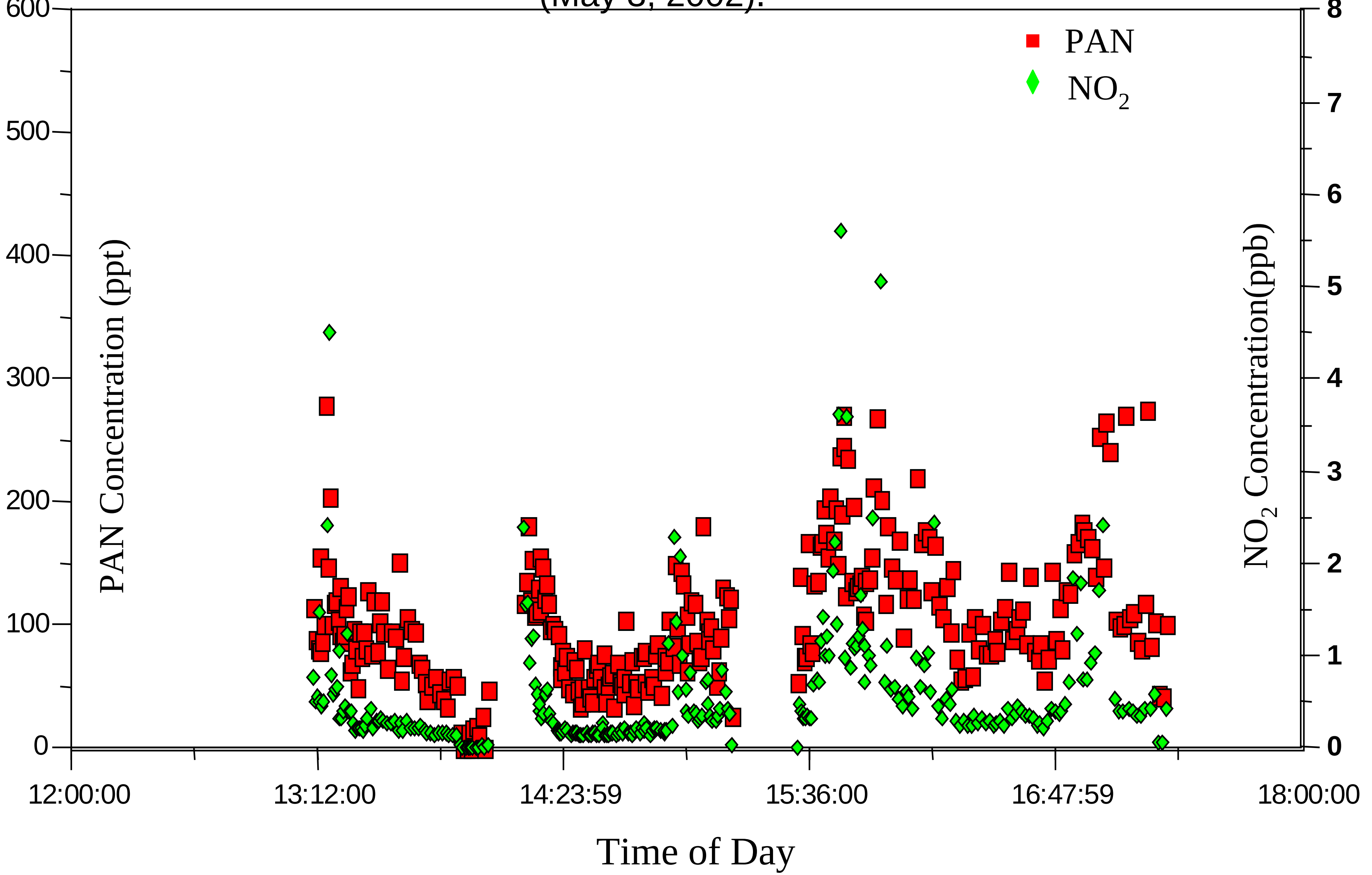


The ratio of peak areas for PAN/NO2 gives a relative sensitivity of 1.4


Comparison of raw NO_2 Signals
Luminol Chemiluminescence -
Ozone Chemiluminescence with Catalytic Conversion -
Ozone Chemiluminescence with Photolytic Conversion -
PEAK AREA (counts)
1.50E+7
1.00E+7
5.00E+6
0.00E+0
12
10
8
6
4
2
0
VOLTS
2:24:00 PM
3:36:00 PM
4:48:00 PM
TIME

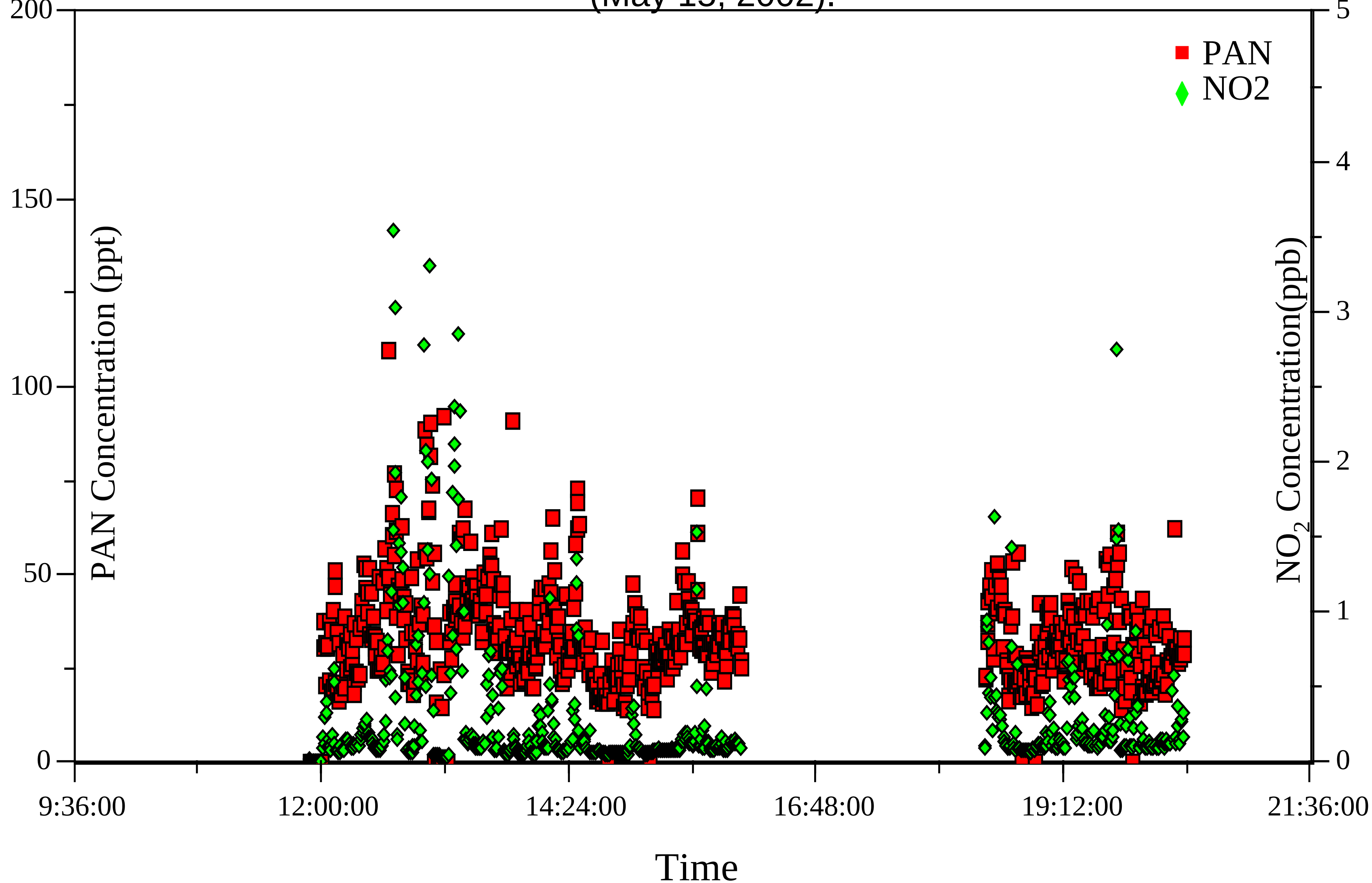
Typical NO_2 and PAN profiles obtained over the Tampa area during the Bay Region Atmospheric Chemistry Experiment (BRACE)

(May 3, 2002).



Typical NO_2 and PAN profiles obtained over the Western Boundary during the Bay Region Atmospheric Chemistry Experiment (BRACE)

(May 15, 2002).



BRACE 05/02 Summary of Twin Otter PAN results.

Date	Max (ppt)	Avg (ppt)	Median (ppt)	Detection Limits	Objective
May 1	185	51	39	10	Test
May 2	197	46	34	10	Test
May 3	275	103	95	10	Bay Survey
May 6	229	62	52	10	Sea Breeze
May 8	270	51	46	10	Sea Breeze
May 10	196	70	69	25	Urban Plume
May 12	167	43	48	35	Power Plant Plume
May 13	94	12	<30	30	Urban Plume
May 15	110	33	32	15	Gulf
May 17	160	22	<30	30	Gulf/Ground Sites
May 20	188	54	50	20	Urban Plume
May 22	129	40	35	15	Eastern/Western Boundary
May 28	83	31	31	15	Eastern Boundary
May 29	122	36	35	15	Urban Plume
May 30	64	20	19	15	Urban Plume
May 31	104	8	<20	20	Urban plume
June 1	176	61	65	50	Power Plant Plume

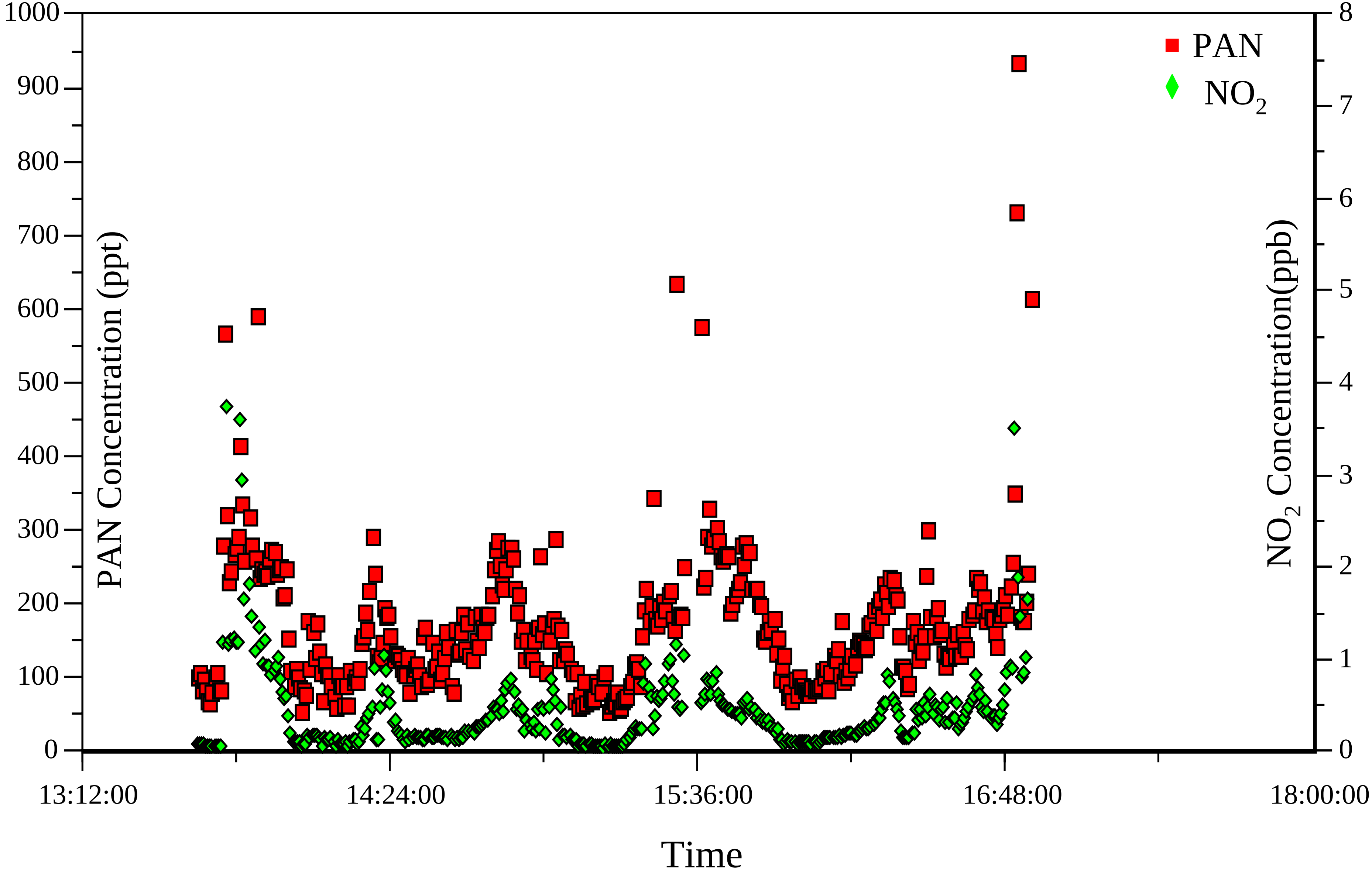
Detection Limits reported in ppt based on a concentration which gives a signal equal to 3 times the standard deviation of baseline values.
PMT replaced on May 21.
High detection limits on June 1 probably due to Luminol decay.

BRACE 05/02 Summary of Twin Otter NO_2 results.

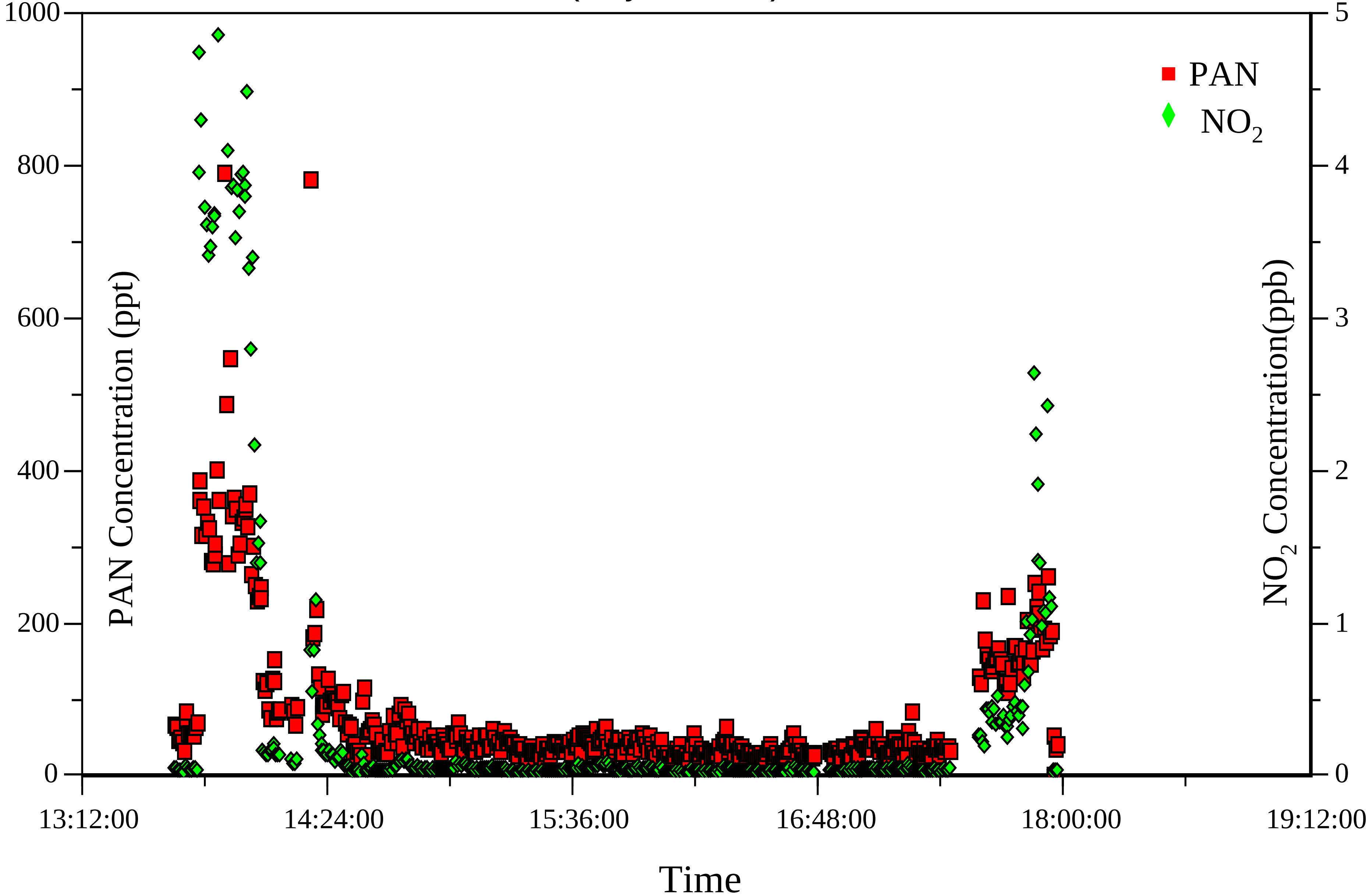
Date	Max (ppb)	Avg (ppb)	Median (ppb)	Detection Limits	Objective
May 1	4.57	0.50	0.11	0.010	Test
May 2	0.273	0.08	0.07	0.010	Test
May 3	16.42	0.91	0.35	0.010	Bay Survey
May 6	8.10	0.38	0.11	0.010	Sea Breeze
May 8	20.44	0.30	0.07	0.010	Sea Breeze
May 10	2.63	0.14	0.11	0.020	Urban Plume
May 12	21.69	0.45	0.12	0.025	Power Plant Plume
May 13	6.11	0.37	0.10	0.020	Urban Plume
May 15	8.62	0.28	0.12	0.010	Gulf
May 17	21.49	0.27	0.07	0.020	Gulf/Ground Sites
May 20	25.71	0.68	0.17	0.015	Urban Plume
May 22	4.00	0.19	0.09	0.010	Eastern/Western Boundary
May 28	6.20	0.13	0.08	0.010	Eastern Boundary
May 29	19.05	0.65	0.09	0.010	Urban Plume
May 30	13.82	0.23	0.05	0.010	Urban Plume
May 31	16.05	0.51	0.07	0.015	Urban plume
June 1	17.11	0.58	0.20	0.036	Power Plant Plume

Detection Limits reported in ppt based on a concentration which gives a signal equal to 3 times the standard deviation of baseline values.
PMT replaced on May 21.
High detection limits on June 1 probably due to Luminol decay.

Typical NO_2 and PAN profiles obtained over the Fresno area during the Central California Oxidant Study (CCOS) (July 9, 2000).



Typical NO_2 and PAN profiles obtained over the Western Boundary during the Central California Oxidant Study (CCOS) (July 8, 2000).



CCOS 07/00 Summary of G1 PAN results.

Date	Max (ppt)	Avg (ppt)	Median (ppt)	Detection Limits	Objective
June 28	225	76	<70	70	Northern Boundary
July 5	1206	150	96	70	Fresno Area, Low Passes
July 5	776	133	106	70	Fresno Area
July 8	2969	71	<70	70	Western Boundary, AM
July 8	2908	91	<70	70	Western Boundary, PM
July 9	798	163	100	70	Fresno Area, Low Passes
July 9	933	169	155	70	Fresno Area
July 10	993	134	94	70	Fresno Area, Low Passes
July 10	2965	231	211	70	Fresno Area
July 11	3065	261	140	70	Fresno Area, Low Passes
July 11	2157	308	191	70	Fresno Area

Detection Limits reported in ppt based on a concentration which gives a signal equal to 3 times the standard deviation of baseline values.

High detection limits due to use of air as carrier.

ACKNOWLEDGMENTS

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The aircraft data taken during the BRACE field campaign.
Was supported by the NOAA Air Resources Laboratory and the Florida Department of Environmental Protection.

CCOS 07/00 Summary of G1 NO_2 results.

Date	Max (ppb)	Avg (ppb)	Median (ppb)	Detection Limits	Objective
June 28	2.03	0.27	0.0.16	0.05	Northern Boundary
July 5	49.80	1.60	0.12	0.05	Fresno Area, Low Passes
July 5	19.00	0.77	0.26	0.05	Fresno Area
July 8	52.73	0.97	<0.05	0.05	Western Boundary, AM
July 8	23.57	0.48	0.05	0.05	Western Boundary, PM
July 9	28.91	1.55	0.14	0.05	Fresno Area, Low Passes
July 9	17.94	0.54	0.29	0.05	Fresno Area
July 10	15.34	0.65	0.12	0.05	Fresno Area, Low Passes
July 10	9.89	0.68	0.41	0.05	Fresno Area
July 11	53.59	3.53	0.195	0.05	Fresno Area, Low Passes
July 11	35.84	1.77	0.343	0.05	Fresno Area

Detection Limits reported in ppt based on a concentration which gives a signal equal to 3 times the standard deviation of baseline values.

High detection limits due to use of air as carrier.